

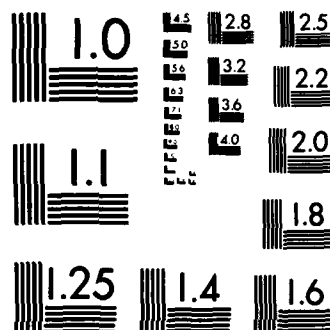
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"Basic Studies of Ion Mixing"

ANNUAL PROGRESS REPORT

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Principal Investigators: Professor Marc-A. Nicolet
(818) 356-4803
Dr. Bruce M. Paine
(818) 356-6555

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This is a progress report for the project 'Basic Studies of Ion Mixing', after the first year of a three - year contract. The major objectives of this work are (A) to identify systematic trends that reveal the important parameters of ion beam mixing, and (B) to investigate the relationship between the mechanisms of ion mixing and thermal processing. To date, 14 papers on this work have been published, or submitted for publication. These are listed as an appendix to this report; they are referenced by number in the text.

A. Mechanisms of Ion Mixing

A.1. Effect of Chemical Driving Forces.

We have observed a correlation between the amount of low temperature ion mixing of metallic bilayers and the calculated heats of mixing of the corresponding binary alloys (3). For these experiments, layers of Pt or Au were mixed with a variety of 3d metals (Ti, V, Cr, Mn, Co and Ni). The amount of mixing was quantified as $4Dt/\phi$ where Dt is the square of the observed diffusion length and ϕ is the irradiation fluence. The heats of mixing, $-\Delta H_m$, were taken from published calculations for binary alloys, assuming a 1:1 abundance ratio. We found that $4Dt/\phi$ scales roughly linearly with $-\Delta H_m$ for the Au/(3d metal) couples and the Pt/(3d metal) couples.

By contrast, in thin marker metal/metal systems, we have found no correlation with heats of mixing (work not yet submitted for publication.) Thus in metal/metal systems, the chemical driving forces are important in situations where finite quantities of both components are available, but not when one component is highly diluted.

In a comprehensive survey of all known marker experiments

prior to these (4) we found widely different results for semiconductor/metal systems. These cannot be easily explained at present.

A.2. Effect of Heat of Sublimation.

In addition to chemical forces, one would expect ion beam mixing to depend on the energy required to displace atoms from lattice sites. A convenient measure of this energy is the elemental sublimation energy. To test this, we have measured the mixing at low temperatures of a series of 5d/4d metal bilayers, each with $\Delta H_m = 0$, and roughly the same elemental sublimation energies (1,3). We find that $4Dt/\phi \sim (-\Delta H_m)^{-2}$.

Together with Dr. W. L. Johnson of Caltech, we have postulated a universal equation for low temperature mixing of metal/metal systems by dense collision cascades (3). It is based on the thermal spike model of Vineyard and gives $4Dt/\phi$ in terms of ΔH_m and the cohesive energy, which can be related to sublimation energies. Constants in the equation were found by fitting the data for metal-metal bilayers.

We have tested these ideas with an extensive series of marker experiments (as yet not written up) and found generally good agreement with the model.

B. Relation Between Ion Mixing and Thermal Processing

B.1. Search for Dominant Moving Atomic Species in Formation of Silicides.

These experiments have been conducted by measuring the shifts of inert marker layers (Mo or W) resulting from growth of silicide. Similar experiments are currently being conducted, with different



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markers, by L. S. Hung at Cornell University. Since such measurements are difficult and may be disrupted if the marker influences the reaction, it is very desirable to have them confirmed by work in different labs., with different marker elements. The results to date are summarized in the following table:

Compound	Moving Species		Ref. for Ion Mixing Result
	Thermal Processing	Ion Mixing	
Pd_2Si	Si	Si	Hung et al.
CrSi_2	Si	Si	13, 14, Hung et al.
Ni_2Si	Ni	Si, Ni(2:3)	13, 14, Hung et al.
Pt_2Si	Pt	Si, Pt(3:2)	13, 14

We observe that Si moves in all of the systems investigated so far with ion mixing. By contrast, it is only the metal atoms that move in conventional thermal growth of Ni_2Si and Pt_2Si . However high temperature thermal growth of these silicides, as well as all the refractory metal silicides, is known to involve motion of Si atoms. We therefore speculate that the mechanism of metal silicide growth by ion mixing is similar to that of high temperature thermal growth. Indeed, the idea of momentary elevation of small volumes to high temperatures is central to the thermal spike model, which we have shown to be quite successful (3).

B.2. Metal - Metal Systems.

These will be addressed in future work.

C. Other Related Studies

We have also performed several studies which, though not

directly outlined in the contract proposal, are relevant to the basic understanding of ion beam mixing.

C.1. Reviews.

Three extensive reviews of the subject of ion beam mixing have been prepared, with partial support of this contract (4,8,12).

C.2. Preferential Sputtering.

Thick layers of CoSi_2 and NbSi_2 were sputtered with 200 - 260 keV Xe ions and analysed by backscattering spectrometry (2).

Preferential sputtering of the silicide gives rise to depletion of Si atoms near the surface. This depleted region is substantially thinner for irradiations at 200 deg C than for those at room temperature. We take this to be strong evidence for atomic motion by radiation - enhanced diffusion under bombardment at the higher temperature.

C.3. Ion - Induced Mixing in Ni - SiO_2 Bilayers.

This work is part of an on-going study designed to give information on the basic mechanisms of ion beam mixing of metal/ceramic systems. 250 Å Ni films are evaporated onto SiO_2 substrates and irradiated with 300 keV Xe ions. In earlier work, the mixing in the SiO_2 has been examined by backscattering spectrometry, after etching of the un-mixed Ni. Long range (> 500 Å) recoil mixing was readily identified. But mixing at shallower depths in the SiO_2 was not so easily understood: it showed evidence of collision cascade character, but also showed a strong temperature dependence. We have now studied the region within 500 Å of the surface more closely by means of cross sectional TEM and ESCA (5). We find that Ni atoms in the SiO_2 after room temperature mixing, are mostly incorporated in a 50 Å band lying about 50 Å below the surface, and exist as oxide

clusters. After mixing at high temperatures (750 K) this band is not observed. We model the phenomenon as follows: during the initial collisional regime the cascade is "hot" enough that all the constituents are miscible and Ni diffuses into the SiO_2 . As the cascade cools, the Ni concentration exceeds the instantaneous equilibrium level in SiO_2 and some is segregated to the surface. For the mixing at high temperatures, the segregation diffusion parameter is large enough that Ni from deeper regions is also expelled.

C.4. Formation Kinetics of Metal Silicides.

In the study of thermal growth of metal silicides, square root kinetics are usually taken to indicate diffusion - limited processes, while linear kinetics are thought to be evidence for interface reaction - controlled processes. Since the mechanisms for silicide growth by ion beam mixing are thought to be the same as for thermal growth, one might naturally advance the same interpretation for the ion beam mixing kinetics. We have tested this idea by exploiting the fact that in ion beam mixing one can arrange the experiment so that the beam mixes only one interface, or the other, or both (9). The results are as follows:

Silicide	Kinetics Observed		Mixed Interface	Does Silicide Grow?
	Ion Mixing	Thermal		
CrSi ₂	linear	linear	Cr/CrSi ₂	Yes
			Si/CrSi ₂	No
			Both	Yes
Pt ₂ Si	sqr. rt.	sqr. rt.	Pt/Pt ₂ Si	No
			Si/Pt ₂ Si	No
			Both	Yes
TaSi ₂	-	linear	Ta/TaSi ₂	No
			Si/TaSi ₂	No
			Both	Yes

The observations for CrSi₂ and Pt₂Si are consistent with the known ion beam kinetics; kinetics have not been reported for TaSi₂. The results reveal that it is the Cr/CrSi₂ interface which controls the growth of CrSi₂ by ion beam mixing.

C.5. Oxidation of CoSi₂.

We have attempted to use ion mixing to suppress the undesirable island formation that is observed in the oxidation of CoSi₂ (7). This oxidation technique is being explored in our laboratory as a method for forming high conductivity metal interconnects for integrated circuits. It was thought that ion mixing of the silicide with the substrate might improve adhesion and hence improve the lateral uniformity of the film. Indeed the method was successful under some circumstances.

C.6. Crystalline Structures of Phases Formed by Ion Beam Mixing of

Multilayer Systems.

Ion beam mixing of metal/metal multilayer structures leads to formation of both crystalline and amorphous alloys, depending on the composition of the film after mixing. According to the "Structural Difference Rule" proposed by us in earlier work, the alloy will most likely be amorphous if the average composition lies in a two - phase region of the phase diagram, and the two constituent elements have different elemental crystal structures. The rule made no statement about the situation when the constituent elements have the same crystal structures. We have now studied two such systems, namely Ru - Zr and Ru - Ti (6,10), in which the terminal elements all have hcp structure. We find that amorphous phases form at stoichiometries of $\text{Ru}_{25}\text{Zr}_{75}$ and $\text{Ru}_{75}\text{Zr}_{25}$, mixed at room temperature or below. However we note that an intermetallic compound, ZrRu , with bcc structure, divides the Ru - Zr phase diagram. Thus the Structural Difference Rule can be extended to predict amorphous phases when the average composition lies in a region of the phase diagram bounded by compounds with differing crystal structures, as well as elements with different structures.

For Ru - Ti, we do not observe the corresponding amorphous phases, even though the phase diagram is essentially the same. This clearly violates the extended rule. We have developed a physical model to explain the rule and observations (3). We discuss these two systems in terms of this model in publication (6).

C.7. Defect Production by Implantation in CrSi_2 .

We have monitored the electrical resistivity of CrSi_2 thin films as a function of irradiation fluence, and identified changes associated with defect generation and recombination (11).

Appendix. Publications

1. Correlation between Cohesive Energy and Mixing Rate in Ion Mixing of Metallic Bilayers

M. Van Rossum, Y-T. Cheng, M-A. Nicolet and W. L. Johnson, Appl. Phys. Lett. 46 (1985) 610.

2. Temperature Dependent Preferential Sputtering in CoSi_2 and NbSi_2

K. A. Affolter, A. H. Hamdi and M-A. Nicolet, Appl. Phys., to be published, 1985.

3. When is Thermodynamics Relevant to Ion-Induced Atomic Rearrangements in Metals?

W. L. Johnson, Y. T. Cheng, M. Van Rossum and M-A. Nicolet, Invited paper presented at the 4th International Conference on Ion Beam Modification of Materials, Ithaca New York (July 16-20, 1984), Nucl. Instr. Meth. Phys. Res. B7/8 (1985) 657.

4. Ion Beam Mixing: Basic Experiments

B. M. Paine and R. S. Averback, Invited paper presented at the 4th International Conference on Ion Beam Modification of Materials, Ithaca New York (July 16-20, 1984), Nucl. Instr. Meth. Phys. Res. B7/8 (1985) 666.

5. Ion-Induced Mixing in Ni-SiO_2 Bilayers

T. C. Banwell, M-A. Nicolet, P. J. Grunthaner and T. Sands, Paper presented at the Materials Research Society Symposium on Energy Beam-Solid Interactions and Transient Thermal Processing, Boston, Massachusetts (November 26-30, 1984), Mat. Res. Soc. Symp. Proc. Vol. 35 (1985) 545.

6. Amorphous and Crystalline Phase Formation by Ion-Mixing of Ru-Zr and Ru-Ti

Y-T. Cheng, W. L. Johnson and M-A. Nicolet, Paper presented at the Materials Research Society Symposium on Layered Structures, Epitaxy and Interfaces, -Boston, Massachusetts (November 26-30, 1984), Mat. Res. Soc. Symp. Proc., to be published, 1985.

7. Experimental Investigations on the Oxidation of Cobalt Disilide (CoSi_2)

S.-J. Kim, T. C. Banwell, R. Shima and M-A. Nicolet, Paper presented at the SPIE Conference on Advanced Applications of Ion Implantation, Los Angeles, California (January 23-25, 1985), SPIE Proceedings Vol. 530, M. I. Current and D. K. Sadana, eds. (SPIE, 1985), p. 152.

8. Ion Beam Mixing in Si Systems

B. M. Paine, Invited paper presented at the SPIE Conference on Advanced Applications of Ion Implantation, Los Angeles, California (January 23-25, 1985), SPIE Proceedings Vol. 530, M. I. Current and D. K. Sadana, eds. (SPIE, 1985), p. 114.

9. Investigation of Formation Kinetics of CrSi_2 , TaSi_2 and Pt_2Si by Ion Beam Mixing

F. C. T. So, U. Shreter and M-A. Nicolet, Paper presented at the SPIE Conference on Advanced Applications of Ion Implantation, Los Angeles, California (January 23-25, 1985), SPIE Proceedings Vol. 530, M. I. Current and D. K. Sadana, eds. (SPIE, 1985), p. 145.

10. Studies on the Rules for Amorphous Phase Formation by Ion-Mixing in Metallic Systems

Y-T. Cheng, W. L. Johnson and M-A. Nicolet, Paper presented at the SPIE Conference on Advanced Applications of Ion Implantation, Los Angeles, California (January 23-25, 1985), SPIE Proceedings Vol. 530, M. I. Current and D. K. Sadana, eds. (SPIE, 1985), p. 134.

11. Xenon Irradiation-Induced Changes in CrSi_2 Thin Films

X-A. Zhao, T. C. Banwell and M-A. Nicolet, Paper presented at the SPIE Conference on Advanced Applications of Ion Implantation, Los Angeles, California (January 23-25, 1985), SPIE Proceedings Vol. 530, M. I. Current and D. K. Sadana, eds. (SPIE, 1985), p. 127.

12. Ion Beam Mixing

B. M. Paine and B. X. Liu, Chapter in "Materials Surfaces. Part A - Modification", C. R. Clayton and J. B. Lumsden, eds. (Academic, New York), to be published, 1985.

13. Moving Species in Pt_2Si , Ni_2Si and CrSi_2 Formed by Ion Mixing and Thermal Annealing

X. A. Zhao, K. Affolter and M-A. Nicolet, Paper presented at the Materials Research Society Symposium on Thin Films, San Francisco, California (April 15-18, 1985), Mat. Res. Soc. Symp. Proc., to be published, 1985.

14. Transition-Metal Silicides Formed by Ion Mixing and by Thermal Annealing: Which Species Moves?

K. Affolter, X. A. Zhao and M-A. Nicolet, submitted to J. Appl. Phys.

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